Relation of Slag Viscosity and Surface Tension to Sintering Potential

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The purpose of this paper is to discuss the relative effect of viscosity and surface tension on sintering potential or agglomeration in coal utilization systems. Of specific interest is the effect of composition and atmosphere on viscosity and surface tension.

BACKGROUND

Sintering is the process by which individual particles or ash particles and slag bind together to form a compact mass. The mechanisms by which sintering occurs are: viscous flow, vapor condensation, diffusion, and surface tension (1,2). Raask (3) has shown that, for coal utilization systems, the major mechanism is that of viscous flow with a reactive liquid phase. The extent of sintering, given by the square of the radius of the contact area (x^2) for a given time, t, is defined by the Frenkel model (3):

$$x^2 = \frac{3\,\gamma\,rt}{2\eta} \tag{1}$$

where r is the initial particle radius, γ is the surface tension of the liquid phase, and η is the viscosity of the liquid phase. According to the Frenkel model, the extent of sintering is inversely proportional to the viscosity of the liquid phase and proportional to the surface tension. It is known that viscosity and surface tension are dependent on composition and atmosphere. Figure 1 (after Raask) shows the variation of surface tension , viscosity, and the rate of sintering with respect to temperature.

It must be noted that the Frenkel model is based on studies in which particles are in intimate contact with one another prior to heating. Sintering then occurs, in the case of ash species, with the formation of a liquid phase on the particle surface. In coal utilization systems, the particles are not in intimate contact with one another but are in constant relative motion. Therefore, the process of sintering or agglomeration only begins when particles collide and adhere to each other or to a slag layer. During initial contact the surface tension of the respective surfaces can play a rate-limiting role as it affects the adhesion of ash particles. The lower the surface tension of the liquid phase on the particle surface the greater the degree of adhesion and sintering resulting in either a fairly strong or large agglomerate. If the surface tension of the molten phase is sufficiently high initial adhesion may be limited. This would also be the case for particles with low viscosity liquid phases. If two particles collide, each having liquid phases of relatively high viscosity and low surface tension, initial adhesion can occur which could lead to some degree of agglomeration. However, the extent of sintering would be limited resulting in a relatively weak agglomerate (4).

To account for the non-static condition of ash particles relative to one another a modification of the Frenkel model is used (4):

$$x^2 = f\left[\frac{1}{\gamma}, t_1, r, \frac{1}{\eta}\right] \frac{3\gamma t_2}{2\eta}^4 \tag{2}$$

where t_1 refers to the contact time and t_2 refers to time after the initial contact. The function term indicates that as the probability and extent of initial adhesion approaches zero (high surface tension) then the degree of sintering will approach zero. However, after t_1, the degree of sintering will follow the Frenkel model

(Equation 1). In the probability function surface tension is inversely related to rate, whereas, in the Frenkel model the rate is proportional to the surface tension. The reason for this is that at initial contact the higher the surface tension the less the liquid "wets" the adjacent surface. After the formation of a "neck" or liquid bridge between particles (after t_1) surface tension pulls the liquid material from the convex surface to the concave surface at the region of the neck. With increasing surface tension the force with which adhesion of the particles occurs increases. So the case is made that surface tension does initially affect the critical adhesion of particles in the agglomeration process. However, after adhesion, the rate of sintering is governed by the viscosity of the molten phases present on the particle surface.

EXPERIMENTAL

Ash samples used in both viscosity and surface tension determinations were produced from coal samples pulverized to -60 mesh and then ashed for three hours at 1000°C. Each sample was ashed in an oxidizing atmosphere and a reducing atmosphere of 8% hydrogen in nitrogen. The ash samples were then analyzed by X-ray fluorescence to determine bulk chemical composition.

A Haake RV-2 Rotovisco (rotating bob viscometer) unit was used for viscosity determinations. Each sample was heated to 1450°C and soaked for several to ensure complete melting. A cool down cycle was then initiated with readings taken every 10°C. The sample was equilibrated for 20 to 30 minutes at each temperature when viscosity measurements were made.

To determine surface tension a sessile drop method was used. A sample of ash was pressed into a pellet, weighed, and centered on a plaque of relatively nonreactive vitreous carbon. During heating a slag bead is formed upon melting of the ash pellet. The bead shape is determined by the surface tension forces between the liquid, gas, and solid phases. Therefore, the sessile drop technique requires geometric definition of the bead at any one temperature. The pellet image was photographed at 1000°C and 1200°C and then at 5°C intervals until the ash pellet was completely melted or a temperature of 1400°C was reached.

The computer method used to calculate surface tension was proposed by Maze and Burnet (5,6). The advantage of this technique is that a series of measurements from photographs are used to define the bead shape to calculate surface tension rather than relying on one measurement, as in the case of contact angle, thereby reducing measurement error. For a more detailed discussion of this technique refer to Miller (4) or Maze and Burnet (5,6).

RESULTS AND DISCUSSION

Relation of Viscosity to Atmosphere and Composition

Work conducted at the Bituminous Coal Research National Laboratory and the University of North Dakota Energy and Mineral Research Center (UNDEMRC) has shown that there are differences in slag behavior in oxidizing, reducing, and inert atmospheres (4). The results show that slag viscosity is decreased under reducing conditions and increases under oxidizing conditions as in the case of the Baukol-Noonan coal slag in Figure 2.

In general, ash melts can be classified as silicate melts. The compositional components can be described as follows: glass formers (SiO_2 and P_2O_5), modifiers (CaO, MgO, Na_2O, and K_2O), and amphoterics (Al_2O_3 and Fe_2O_3). Glass formers tend to enhance polymerization of the melt while modifiers tend to disrupt polymerization. The amphoterics can act either as glass formers or modifiers (4). For high-silica slags the important factor in determining viscosity is the ratio of SiO_2 to modifiers. Large amounts of network formers (silica) result in a higher degree of polymerization, a rapid rate of nucleation and crystallization. This behavior produces liquid phases having higher viscosities resulting in a decreased potential for sintering.

The viscosity behavior of low-silica slags is governed by the ratio of CaO to modifiers or alkalies. Alkalies tend to inhibit silica polymerization by weakening the bonds between silica tetrahedra. Alkalies, as modifiers, also increase the rate of crystal growth by reducing viscosity thereby permitting more rapid diffusion of ions to the crystal front. Such liquid phases of low viscosity present during the ash phase would increase the potential of sintering.

Viscosity tests where additions of calcium and sodium were made to intermediate to high-silica slags show a decrease in the viscosity at all temperatures. The result of decreasing viscosity of a liquid phase is to enhance the rate of sintering or potential for agglomeration of ash particles producing a liquid phase of high alkali composition.

Effect of Atmosphere on Surface Tension

Results from three different coal slag surface tension tests conducted under oxidizing and reducing atmospheres are illustrated in Figure 3. Each point is labeled to identify the coal slag and the atmosphere under which the test was performed: Gascoyne Red (GRR, GRO), Gascoyne Blue (GBR, GBO) and Beulah (BSR, BSO) where "O" refers to oxidizing and "R" refers to reducing conditions. The oxidizing and reducing tests for each slag are connected with a straight line. In general, the surface tension of a slag is greater in a reducing atmosphere versus an oxidizing atmosphere. In addition, the temperature at which the ash pellet becomes completely liquid is higher in oxidizing atmospheres than in reducing atmospheres. Assuming a constant composition, viscosity decreases under reducing environments while surface tension increases. Given these facts the potential for sintering is enhanced in reducing versus oxidizing environments.

Relation of Surface Tension to Composition and Viscosity and Its Effect on Sintering

As previously discussed, surface tension and viscosity are important in governing the rate of sintering and the tendency of particles to agglomerate. Both surface tension and viscosity decrease with temperature while the rate of sintering increases (Figure 1). However, the rate of sintering shows an inverse relationship with viscosity and direct relationship with surface tension (Equation 2). Therefore, it is necessary to determine how viscosity and surface tension change relative to one another with changes in temperature and composition.

A series of fifteen low-rank coal slags were studied as to viscosity, surface tension, and bulk composition as shown in Table 1. Of particular interest is the relationship of silica and sodium oxide to surface tension because of their prevalence in coals, agglomerates, and ash deposits, and their effect on viscosity. While fouling tendency may not be considered to be a rigorous measure of sintering it has some merit in this study. The adhesion and sintering of ash particles in a fouling deposit is produced under dynamic conditions where the relative motion of ash particles occurs along with impaction. As discussed earlier, the process of sintering begins when particles collide and adhere to each other. Therefore the initial adhesion of particles is an important step in initiating sintering. In a standard sintering test, the ash particles are packed and heated in a static conditions where no consideration of relative motion or impaction of ash particles occurs. Ashes which tend to agglomerate are designated with an "-H" or "-M" for high or moderate agglomerating tendency, respectively. Ashes which displayed a low tendency to foul or agglomerate are designated with an "-L". The classification is qualitative and determined by pilot-scale combustion and deposition results.

In general, slags having higher silica content tend to have higher surface tension while slags high in sodium content have lower surface tensions. Figure 4 is a plot of the ratio of the mole fraction of SiO_2 to Na_2O as a function of surface tension. There is a separation between those ashes which have a lower tendency to agglomerate and those ashes which tend to agglomerate. This data along with viscosity data suggests that increased silica oxide content increases both surface tension and viscosity. An increase in sodium oxide content decreases both viscosity and surface tension. Figure 4 shows those coals characterized as low agglomerating ashes having increased silica content and higher surface tensions. Conversely, coals with increased sodium content have lower surface tension but have increased fouling and agglomerating tendency. These results seem to be contrary to the relations in Equation 1. Therefore the effect on sintering due to compositional variations must be due to the relative change in surface tension and viscosity with composition.

To determine the relationship of surface tension and viscosity as it varies with composition it was decided to use a combination of experimental surface tension data with calculated viscosity values. The following assumptions were made in the Frenkel model:

o The particle radius (r) and time (t_2) were assumed to be constant. Therefore x^2 is proportional to $\gamma\eta$.

o A modified version of the Urbain equation developed by Kalmanovitch (7) was used to calculate the viscosity of the molten phases at the temperature at which each surface tension measurement was taken. The equation used was based on its successful application in predicting viscosities in previous studies (4).

In Figure 5 a plot of the calculated viscosities versus surface tension reveals some separation of low- and high-fouling coals. In general, the ratio of surface tension to viscosity is related to sintering potential (Equation 2). Those ashes observed to have low agglomerating behavior have low surface tension to viscosity ratios. Those ashes which tend to exhibit agglomeration have larger surface tension to viscosity ratios.

CONCLUDING REMARKS

The discussion here suggests the following relationships:

o Slag viscosity decreases while surface tension increases under a reducing atmosphere. The net result is increased sintering potential of an ash in a reducing versus oxidizing environment

o An increased silicon dioxide content increases the viscosity of a slag at a greater rate than the surface tension of the slag. The net result is reduced sintering.

o An increased sodium oxide content (possibly total alkali content) decreases the viscosity of a slag at a greater rate than the slag surface tension. The net result is an increase in sintering.

o Those ashes which tend not to sinter or agglomerate form molten phases which have higher viscosities relative to their surface tension at a given temperature and those ashes which tend to agglomerate form molten phases which have lower viscosities relative to their surface tension at a given temperature.
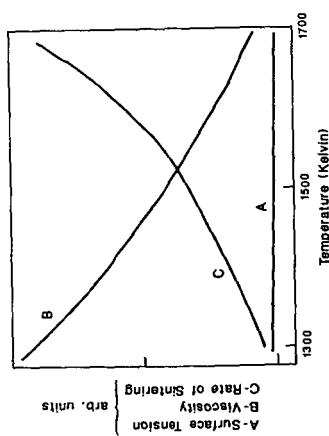
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ACKNOWLEDGEMENTS

Table 1. Chemical Composition of Sample Coal Slags
(Analysis by X-Ray Fluorescence)

Coal	ID	Oxide Weight Percent									
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3
Beulah High Sodium	BH	16.4	12.7	12.9	1.3	1.7	27.0	8.6	19.4	0.0	0.0
Beulah Low Sodium	BL	24.3	16.4	21.2	1.1	1.2	21.2	10.1	4.0	0.3	0.0
Gascoyne Blue	GB	28.8	16.5	5.3	0.0	0.0	22.5	10.7	8.9	0.5	0.0
Gascoyne Red	GR	37.0	12.5	9.6	0.0	0.0	27.0	9.9	3.5	0.6	0.0
Indianhead	IH	33.8	20.9	10.0	0.9	0.3	20.2	4.9	2.8	0.9	5.2
Indianhead	IHO	36.0	22.1	2.8	1.2	0.1	24.0	5.8	1.9	0.9	5.2
Martin Lake	ML	32.9	17.2	7.5	1.7	0.0	25.8	6.2	4.5	0.4	3.8
Martin Lake	MLO	33.3	19.0	10.4	1.2	0.0	24.9	5.9	1.5	0.4	3.3
Pittsburgh 8	P8	46.0	21.8	20.3	1.2	0.3	5.4	1.1	0.0	2.4	1.5
Pittsburgh 8	P8O	49.4	20.6	17.8	1.3	0.2	5.1	1.1	0.0	2.7	1.7
Rosebud McKay	RM	41.3	24.3	6.4	1.5	0.8	18.2	6.7	0.8	0.0	0.0
Velva	VE	23.6	11.4	7.9	0.9	0.4	35.9	9.8	1.6	0.2	8.4
Velva	VEO	24.7	22.8	7.4	0.7	1.1	20.2	5.1	3.2	0.6	14.3
Wyodak	WY	46.8	23.4	3.3	1.6	0.5	15.0	3.4	1.0	0.4	4.5
Wyodak	WYO	41.2	20.0	4.6	2.0	0.8	24.1	5.3	1.0	0.5	0.5

Figure 2. Effect of Atmosphere on Baukol-Noonan Slag Viscosity

$$x^2 = \frac{3rt}{2\eta}$$

where x = radius of the interface assumed to be circular
r = radius of the spherical particles
γ = surface tension
t = time
η = viscosity

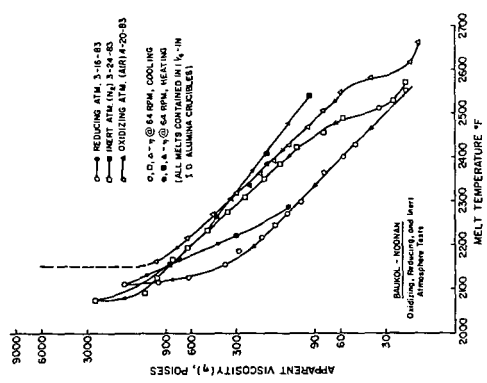Figure 1. Relation of Surface Tension and Viscosity to Sintering as a Function of Temperature
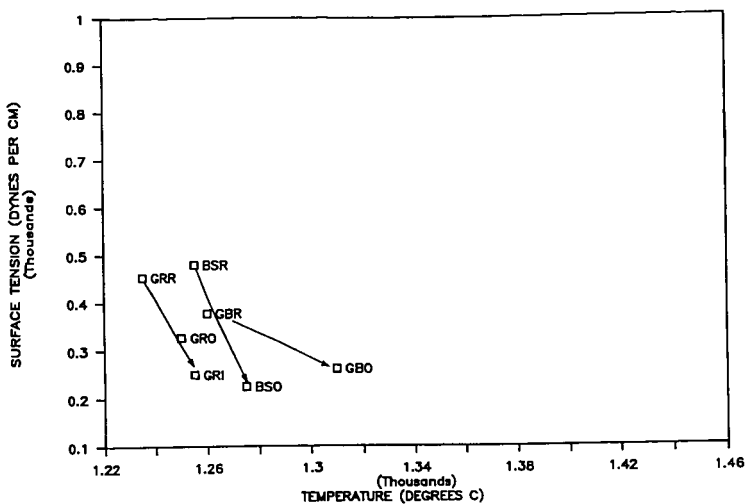
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Figure 3. Effect of Atmosphere on Slag Surface Tension
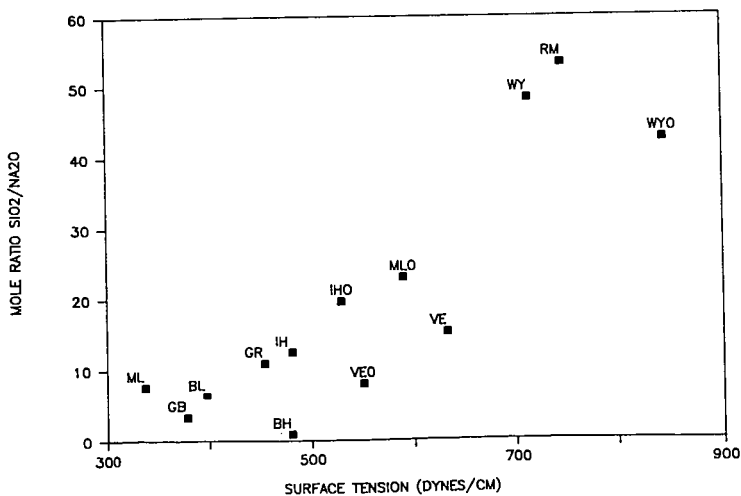
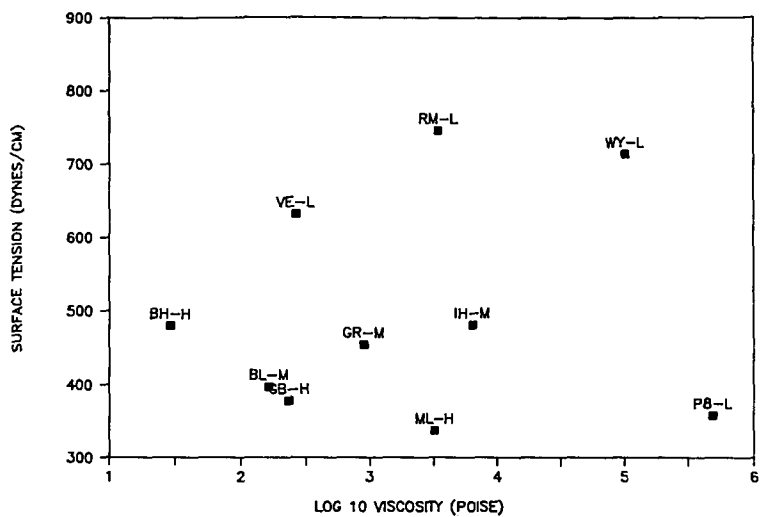**Figure 4. Coal Slag Surface Tension Versus Mole Ratio SiO$_2$/Na$_2$O.**

Figure 5. Calculated Viscosity (Log 10 η) Versus Measured Surface Tension